丙酮－乙醇－丁醇混合物向长链酮醇的高选择性转化

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摘要：近年来随着石油资源的枯竭和环保意识的增强，如何实现以具有环境友好、可再生等诸多优势的生物质资源替代传统化石能源制备燃料和化学品，已经成为了学术界和工业界共同关注的焦点。生物质向生物基化学品和生物基燃料的催化转化过程中，催化材料的水环境下的稳定性一直是该领域的难点。例如丙酮–丁醇–乙醇发酵液（ABE）向生物基液体燃料的催化转化过程中，目前报到的最优的非均相催化材料为金属纳米颗粒负载的镁铝水滑石（M-HT），但是基于水滑石材料特有的结构记忆效应，该催化材料要求初始反应物中水含量不得超过 0.5wt%，急剧增加了上游分离工艺的成本和操作难度。为了解决此共性问题，在我们的工作中，以丙酮–丁醇–乙醇发酵液向生物基液体燃料的催化转化为目标体系，设计了新型催化材料——氧化镁–二氧化硅混合氧化物负载金属纳米颗粒（M-MgO–SiO_2），并系统地考察了金属元素种类（Ni，Cu，Fe，Zn 和 Co）和负载量以及反应温度对其催化活性的影响。研究结果表明，镍负载量为 10 wt%的 Ni-MgO–SiO_2 催化剂具有最优活性：在 240 ℃下反应 20 h 后 C5–C15 的醇酮收率为 81.5%。和预期一致，相比于水滑石系催化剂，该催化剂表现出了良好的耐水性：初始反应物中水含量为 3 wt%时，转化率和产物分布完全不受影响。XRD 和 ^{29}Si MAS NMR 结果显示形成的硅酸镁结构对于提高催化材料的耐水性发挥了重要作用。通过考察 10 wt% Ni-SiO_2，10 wt% Ni-MgO 以及 10 wt% Ni-MgO–SiO_2 的催化活性，揭示了氧化镁和氧化硅的作用。

关键词：ABE 发酵液；催化转化；耐水性；Ni-MgO–SiO_2 催化剂

Upgrade of acetone–butanol–ethanol mixture to high-value biofuels

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Abstract: Upgrade of acetone–butanol–ethanol (ABE) mixture from biomass to high-value biofuels has aroused an increasing attention. However, reported heterogeneous catalyst, metal-containing MgAl-hydrotalcite (HT), is confronted with a serious water-resistance problem due to inherent memory effect of HT material. Aimed at exploring catalysts with improved water-resistance, metal-containing $MgO–SiO_2$ catalysts were synthesized and evaluated. Investigation on effect of metal types including Ni, Cu, Fe, Zn and Co, metal loading and reaction temperature on catalytic performance indicates that the 10 wt% Ni-$MgO–SiO_2$ catalyst provides the best catalytic performance, giving a yield of 81.5 % to C_5–C_{15} ketones and alcohols at 240 °C. As expected, the catalyst exhibits an excellent water-resistance. It could tolerate up to 3 wt% water, which was much higher than 0.5 wt% over Cu- or Pd-HT as reported. Results from XRD and ^{29}Si MAS NMR analyses indicate that the high water-resistance could be ascribed to the more stable structure of magnesium silicates formed in the catalyst than HT materials. To further study effect of catalyst property on catalytic performance, 10 wt% Ni-SiO_2, 10 wt% Ni-MgO, and 10 wt% Ni-$MgO–SiO_2$ catalysts were investigated and characterized. Results from CO_2-TPD, Pyridine-IR and NH_3-TPD analyses reveal that the catalytic performance is significantly affected by acid–base property. Obtaining a high catalytic performance necessitates a cooperation of enough acidic sites and basic sites.

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